



Thermal expansion adjustable polymer matrix composites with giant negative thermal expansion filler



Koshi Takenaka^{a,b,*}, Masayoshi Ichigo^b

^a Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

^b Department of Crystalline Materials Science, Nagoya University, Nagoya 464-8603, Japan

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ABSTRACT

Polymer matrix composites filled with giant negative thermal expansion (NTE) materials were formed by injection moulding. Antiperovskite manganese nitrides, thermal expansion compensating filler of the composites, exhibit NTE greater than -30 ppm K^{-1} in α (coefficient of linear thermal expansion). This gigantic NTE, several to ten times as large as that of conventional NTE materials, can compensate large thermal expansion of polyamide-imide polymer and thermal expansion of the composites is adjustable in a wide range of α value from positive to even negative. Quantitative analyses reveal that thermal expansion of the composites is less than the estimate based on the volume-weighted sum, which is ascribed to much larger elastic modulus of the nitride filler.

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1. Introduction

Synthetic resin, or polymer, is one of the most familiar materials because of its beneficial features of light weight and high workability, but their large thermal expansion emerges as a shortcoming for which reduction is desired in highly advanced industries. For polymers, the coefficient of linear thermal expansion (CTE) α is at least $30\text{--}40 \text{ ppm K}^{-1}$ or at largest over 100 ppm K^{-1} , which is much larger than those of metals and ceramics in the range of several to 20 ppm K^{-1} . Large thermal expansion of polymers is at present one of the most primary factors suppressing their utility value.

For control of thermal expansion in polymers, polymer matrix composites (PMCs) filled with low-expansion inorganic materials have been designed to date. However, silica (SiO_2) filler, one of the most widely used, has, although low, still positive thermal expansion ($\alpha \sim 0.5 \text{ ppm K}^{-1}$) and hence cannot cancel large positive thermal expansion of polymers. For more active suppression of thermal expansion, we need materials that contract on heating, or *negative* thermal expansion (NTE) materials [1–4]. Beta-eucryptite (LiAlSiO_4) is one of the few practical materials for this purpose, but its NTE is highly anisotropic and the magnitude of the aggregate NTE is at largest -5 ppm K^{-1} , which is not enough for general purposes [1].

Relatively large ($\alpha \sim -9 \text{ ppm K}^{-1}$) and isotropic NTE of ZrW_2O_8 [2] enables us to control thermal expansion to a certain degree. Nevertheless, an extensive practical application is still not realized because of the demerits such as high cost, low stiffness, and existence of a pressure-induced less-negative thermal expansion phase ($\gamma\text{-ZrW}_2\text{O}_8$) [5].

In the field of NTE research, remarkable development has been achieved over the last decade. In particular, after the discovery of gigantic NTE in antiperovskite manganese nitrides Mn_3AN (A: metal or semiconducting element) [6], many giant NTE materials such as $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ [7], $\text{Bi}_{1-x}\text{Ln}_x\text{NiO}_3$ (Ln: lanthanoid) [8,9], and $\text{La}(\text{Fe}, \text{Si}, \text{Co})_{13}$ [10] were discovered successively. The NTE of the antiperovskite manganese nitrides is greater than -30 ppm K^{-1} in α , which can compensate large thermal expansion of polymers and opens a new phase of composite science and technology [11]. Ding et al. [12] and Takenaka et al. [13] reported their attempts to form metal matrix composites (MMCs) containing the antiperovskite and proved that thermal expansion of metals are extremely reduced, even to negative. Huang et al. [14] also reported a pioneer study for reducing thermal expansion of polymers by the antiperovskites. In their study, thermal expansion of epoxy resin was reduced 42% by 32 vol.-%- $\text{Mn}_3\text{Cu}_0.6\text{Si}_{0.15}\text{Ge}_{0.25}\text{N}$ filler loading. Here, we report our attempts to form PMCs filled with antiperovskites by means of injection moulding, which is a conventional manufacturing technique enabling a wide range of industrial applications.

* Corresponding author at: Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan.

E-mail address: takenaka@nuap.nagoya-u.ac.jp (K. Takenaka).

2. Experimental

Thermal-expansion compensators, antiperovskite manganese nitrides Mn_3AN , were prepared by solid-state reactions using powders of Mn_2N and pure element A (A: Zn, Sn, purity: 99.9%, particle size: 30–50 μm) as starting materials [13,15,16]. The obtained nitrides were pulverized in an agate mortar down to 30–60 μm diameter. For thermal-expansion measurements, the obtained nitride powder was sintered using a spark plasma sintering (SPS) furnace (Syntex Lab; SPS Syntex Inc.). Linear thermal expansion $\Delta L(T)/L$ was measured at temperature $T=100\text{--}500$ K using a laser-interference dilatometer (LIX-2; Ulvac). For this class of manganese nitrides, $\Delta L(T)/L$ determined by a dilatometry coincides with the lattice parameters obtained by the neutron diffraction study [17]. The crystal structure was investigated using X-ray powder diffraction (XRD, RINT2000; Rigaku). Specific gravity, or density, was determined by an Archimedes method. The polymer matrix composites were formed by injection moulding (MINI-7; Niigata). Powders of the manganese nitride (particle size: 30–60 μm) and polyamide-imide (AI-polymer; Mitsubishi Gas Chemical) were mixed and extruded into pellets at 280–320 $^{\circ}C$. The obtained pellets were moulded by injection under the following condition: cylinder temperature: 300–320 $^{\circ}C$, mould temperature: 130–150 $^{\circ}C$, extrusion pressure: 80–120 MPa. These parameters were determined with reference to a conventional extrusion condition of polyamide-imide.

3. Results

Fig. 1 displays $\Delta L(T)/L$ for typical NTE manganese nitrides including the thermal-expansion compensators of the present study. The giant NTE of the manganese nitrides was achieved by doping Ge or Sn into A site of Mn_3AN (for example, Mn_3ZnN) as “relaxant” of the sharp volume contraction on heating due to the first-order magnetic transition [18–20]. Therefore, the operating-temperature window ΔT of NTE is limited to a certain T range below the magnetic transition temperature and there is a trade-off between width of the operating-temperature window and magnitude of the negative α . However, we can achieve huge NTE if even a narrow operating-temperature window satisfies purposes. In the case of typical NTE compounds $Mn_{3+x}Zn_ySn_{1-x-y}N$, NTE of $\alpha = -25$ ppm K^{-1} at $T = 280\text{--}365$ K ($\Delta T = 85$ K) is possible in principle [16]. The thermal-expansion compensators of the present study had larger magnitude of negative α , though the operating-temperature windows were narrower: $Mn_{3.25}Zn_{0.5}Sn_{0.25}N$ shows

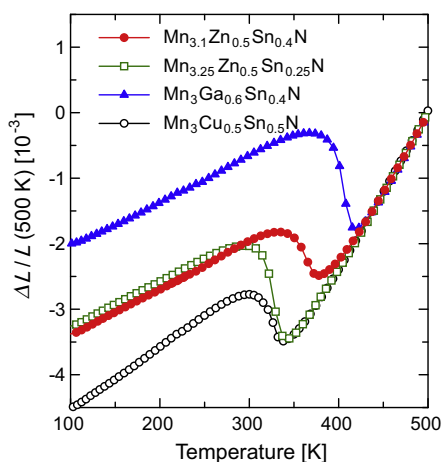


Fig. 1. Linear thermal expansion of typical antiperovskite manganese nitrides showing negative thermal expansion.

NTE of $\alpha = -45$ ppm K^{-1} at $T = 305\text{--}340$ K ($\Delta T = 35$ K) and $Mn_{3.1}Zn_{0.5}Sn_{0.4}N$ shows NTE of $\alpha = -29$ ppm K^{-1} at $T = 335\text{--}375$ K ($\Delta T = 40$ K). These thermal-expansion compensators meet the demand for devices in which the evolution of heat is a problem, including an optical or electronic apparatus.

The matrix of the present composites containing the NTE manganese nitrides is polyamide-imide, which has excellent mechanical properties and relatively low thermal expansion ($\alpha \sim 40$ ppm K^{-1} at room temperature) among polymer materials. The present composite can be formed by injection moulding, conventional processing of polymers. This is the advantage of the present composites over existing low thermal expansion PMCs in which thermal expansion along only a certain direction is reduced by orientation of the filler and/or the polymers. Instead, the present composites enable us to achieve isotropic and three-dimensional control of thermal expansion by existing facilities for injection moulding.

Fig. 2 displays $\Delta L(T)/L$ of 75 wt.-%- $Mn_{3.25}Zn_{0.5}Sn_{0.25}N$ /polyamide-imide composite. Because specific gravities of the matrix and the filler are respectively 1.4 and 6.9, the volume fractions of the matrix and the filler are respectively 62 vol.-% and 38 vol.-% and the specific gravity of the composite is 3.5. The huge NTE of $Mn_{3.25}Zn_{0.5}Sn_{0.25}N$ strongly reduced the thermal expansion of polyamide-imide, resulting in NTE ($\alpha = -3$ ppm K^{-1} at $T = 315\text{--}327$ K) for the composite. Displacement in $\Delta L(T)/L$ is less than 160 ppm at $T = 303\text{--}333$ K, equivalent to the averaged CTE of 5.3 ppm K^{-1} . Huang et al. also reported that the $Mn_3Cu_{0.6}Si_{0.15}Ge_{0.25}N$ filler highly reduced CTE of epoxy resin, but the $\Delta L(T)/L$ of their composites showed rather monotonous T dependence and the remarkable reduction – the negative slope – like the present composites was not confirmed at the T region where the nitride filler exhibited NTE behaviour [14].

Although large difference in the specific gravity between the matrix and the filler might cause uneven distribution of the components, the microscope observation denies it. Fig. 3 is a microscopic image of 38 vol.-%- $Mn_{3.25}Zn_{0.5}Sn_{0.25}N$ /polyamide-imide composite. Matte-gray and glossy-gray regions represent respectively the matrix and the filler. Indeed, we confirmed that the $\Delta L(T)/L$ data obtained on different specimens were identical to each other and they were reproducible after several times repeated thermal cycling. We also confirm that the diameter of the nitride filler is about several 10 μm . This observation also shows that there are not remarkable voids at the interface between the matrix and the filler.

4. Discussion

The obtained thermal expansion of the composites was analysed using models in which particles of an isotropic thermal-expansion-compensating filler are uniformly dispersed in an iso-

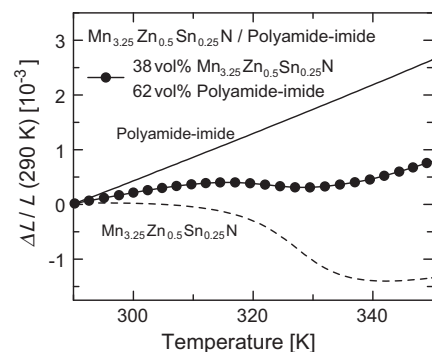


Fig. 2. Linear thermal expansion of 38 vol.-%- $Mn_{3.25}Zn_{0.5}Sn_{0.25}N$ /polyamide-imide composite formed by injection moulding.

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